THE ADDITION OF GRIGNARD REAGENTS TO BENZOYLDURENE

BY

JACK MILLS

A. B., Columbia University, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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Introduction

In earlier studies embracing benzoylmesitylene,[1] benzoylisodurene,[1] benzoyldurene,[2] the mesitoylnaphthalenes,[3] and similar diaryl ketones, it has been demonstrated that addition of Grignard reagents occurs in spite of the excessive crowding about the carbonyl group. The addition may be 1,2, 1,4, or 1,6, depending on the nature of the ketone and of the Grignard reagent which is used. In none of these investigations was the Grignard reagent found to add 1,2 and 1,4 simultaneously to the diaryl ketones, although simultaneous 1,2- and 1,4-addition are observed frequently with α,β-unsaturated aliphatic ketones.

Earlier studies involving the addition of Grignard reagents to hindered diaryl ketones were hampered by the fact that in many cases the products were not crystalline. Since most of the compounds of the diaryl series are relatively high-melting, benzoyldurene was chosen for an exhaustive study of the products resulting from the addition of Grignard reagents to a hindered diaryl ketone.

Experimental and Discussion of Results

It has been found that simultaneous 1,2,- 1,4-, and 1,6-addition occur when benzoyldurene is treated with methylmagnesium iodide under forcing conditions. Five addition products have been isolated from this condensation. The number and type of these addition products depend on the method of decompositon of the Grignard complex and the method employed to separate the products.

1-Duryl-1-phenylethylene (I), m.p. 71-72°, is formed by the dehydrogenation of the tertiary carbinol which results from the 1,2-addition of methylmagnesium iodide. Ozonization of the ethylene yielded benzoyldurene and durylphenylacetic acid. The

olefin was prepared in 15 per cent yield by the condensation of durylmagensium bromide with acetophenone.

The 1,4-addition of the methyl Grignard reagent to benzoyldurene has been demonstrated by the isolation of the enol in the form of its peroxide (II), m.p. 126-128°. Ketonization of the enol with dilute acid yielded 2,3-dihydro-*o*-tolyl duryl ketone (III), m.p. 123-124°. This ketone was dehydrogenated with a palladium-charcoal catalyst to *o*-toluyldurene (IV), m.p. 111-112°. It was also synthesized by the Friedel-Crafts condensation of 2,3-dihydro-*o*-toluyl chloride with durene.

Ketonization of the enol in neutral solution yielded a dihydro-*o*-tolyl duryl ketone (V) m.p. 102°. This ketone was dehydrogenated readily to *o*-toluyldurene (IV) and was quantitatively transformed into another isomeric dihydro-*o*-tolyl duryl ketone (VI), m.p. 117-118°, by platinum.

p-Toluyldurene (VII), m.p. 143-144°, is formed by the spontaneous dehydrogenation of the dihydro-*p*-tolyl duryl ketone which results from the 1,6-addition of methylmagnesium iodide to benzoyldurene. This ketone was prepared by the Friedel-Crafts condensation of *p*-toluyl chloride and durene and also by the reaction of durylmagnesium iodide with *p*-toluyl chloride.

A reduction product, 2,3,5,6-tetramethylbenzohydryl ether, (VIII), m.p. 173-174°, was also formed. This compound had been isolated earlier from a mixture of products obtained by reducing benzoyldurene with sodium amalgam.[4] McKusick[4] isolated another reduction product, m.p. 193-194°, from the reaction of the methyl and phenyl Grignard reagents with benzoyldurene. The structure of this compound has not been established.

Phenylmagnesium bromide has been condensed with benzoyldurene under forcing conditions. Three products have been isolated from the reaction mixture. Although these compounds, m.p. 124-125°, 126-127°, and 161-162°, have not been identified, it seems certain that conjugate addition occurred in this case also.

The condensation of mesitylmagnesium bromide with benzoyldurene yielded only one compound, m.p. 169-170°, presumably the 1,6-addition product.

Bibliography

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[4] McKusick, Thesis, Doctor of Philosophy, University of Illinois, 1944.

Vita

The author was born in New York City on December 22, 1920. After attending the public schools of that city, he entered Columbia College and received the degree of Bachelor of Arts in June, 1941. He entered the University of Illinois as a teaching assistant in the fall of 1941. He held the Carr fellowship during 1942-1943 and since May, 1943, has been employed as a Special Research Assistant.

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